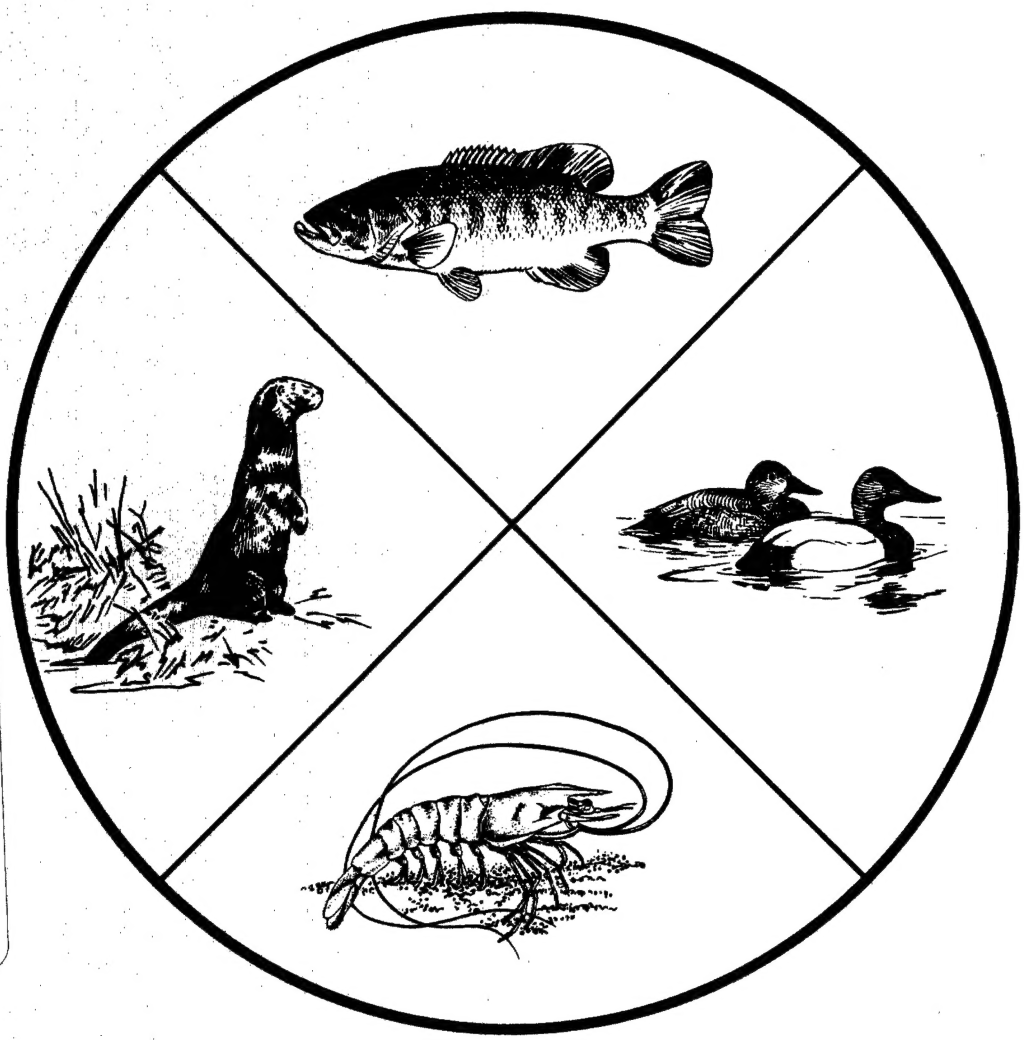
BIOLOGICAL REPORT 85 (1.13)
MARCH 1988

CONTAMINANT HAZARD REVIEWS
REPORT NO. 13

CHLORPYRIFOS HAZARDS TO FISH, WILDLIFE, AND INVERTEBRATES: A SYNOPTIC REVIEW



Fish and Wildlife Service

U.S. Department of the Interior

Other publications in the "Hazards" series[a]

Subject	Publication date	Publication number
Mirex	March 1985	85(1.1)
Cadmium	July 1985	85(1.2)
Carbofuran	August 1985	85(1.3)
Toxaphene	August 1985	85(1.4)
Selenium	October 1985	85(1.5)
Chromium	January 1986	85(1.6)
Polychlorinated Biphenyls	April 1986	85(1.7)
Dioxins	May 1986	85(1.8)
Diazinon	August 1986	85(1.9)
Mercury	April 1987	85(1.10)
Polycyclic Aromatic Hydrocarbons	May 1987	85(1.11)
Arsenic	January 1988	85(1.12)

[a]Copies of individual reviews, if available, can be obtained by writing the Section of Information Management, Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, Maryland 20708.

Biological Report 85(1.13)
March 1988

Contaminant Hazard Reviews
Report No. 13

CHLORPYRIFOS HAZARDS TO FISH, WILDLIFE, AND INVERTEBRATES: A SYNOPTIC REVIEW

by

Edward W. Odenkirchen

Department of Biology
The American University
Washington, DC 20016

and

Ronald Eisler

U.S. Fish and Wildlife Service
Patuxent Wildlife Research Center
Laurel, MD 20708

Fish and Wildlife Service
U.S. Department of the Interior

DISCLAIMER

Mention of trade names or commercial products does not constitute U.S. Government endorsement or recommendation for use.

Suggested citation for this report:

Odenkirchen, E. W., and R. Eisler. 1988. Chlorpyrifos hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish Wildl. Serv. Biol. Rep. 85(1.13). 34 pp.

SUMMARY

Chlorpyrifos (phosphorothioic acid O, O,-diethyl O-(3,5,6,-trichloro-2-pyridinyl) ester), an organophosphorus compound with an anticholinesterase mode of action, is used extensively in a variety of formulations to control a broad spectrum of agricultural and other pestiferous insects. Domestic use of chlorpyrifos in 1982 was about 3.6 million kg; the compound is used mostly in agriculture, but also to control mosquitos in wetlands (0.15 million kg applied to about 600,000 ha) and turf-destroying insects on golf courses (0.04 million kg).

Accidental or careless applications of chlorpyrifos have resulted in the death of many species of nontarget organisms such as fish, aquatic invertebrates, birds, and humans. Applications at recommended rates of 0.028 to 0.056 kg/surface ha for mosquito control have produced mortality, bioaccumulation, and deleterious sublethal effects in aquatic plants, zooplankton, insects, rotifers, crustaceans, waterfowl, and fish; adverse effects were also noted in bordering invertebrate populations.

Degradation rate of chloropyrifos in abiotic substrates varies, ranging from about 1 week in seawater (50% degradation) to more than 24 weeks in soils under conditions of dryness, low temperatures, reduced microbial activity, and low organic content; intermediate degradation rates reported have been 3.4 weeks for sediments and 7.6 weeks for distilled water. In biological samples, degradation time is comparatively short--usually less than 9 hours in fishes, and probably the same in birds and invertebrates.

Chlorpyrifos is acutely toxic to some species of aquatic invertebrates and teleosts at nominal water concentrations ranging between 0.035 and 1.1 ug/l. Acute single-dose oral LD-50 values of chlorpyrifos to susceptible avian species ranged from 5 to 13 mg/kg body weight. Mammals were comparatively tolerant of chlorpyrifos: acute oral LD-50's were reported to be 151 mg/kg body weight, and higher. Lethal dietary concentrations for sensitive species of birds ranged from 30 to 50 mg chlorpyrifos/kg food. Sublethal effects were recorded in all species of organisms examined at concentrations below those causing mortality. These effects included bioconcentration from the medium by teleosts (410X to 1,000X); cholinesterase activity reduction in brain and hematopoietic tissues; reduced growth; impaired reproduction, including sterility and developmental abnormalities;

motor incoordination; convulsions; and depressed population densities of aquatic invertebrates.

Three courses of action are recommended. (1) Restrict the use of chlorpyrifos for mosquito control in wetlands, estuaries, and waterfowl breeding areas because recommended treatment levels are demonstrably harmful to nontarget resident biota. (2) Curtail agricultural use in watershed areas pending acquisition of additional data on chlorpyrifos toxicokinetics. (3) Develop suitable replacements for chlorpyrifos in mosquito control programs; specifically, pesticides with more specificity to target organisms, and lower toxicity to nontarget biota.

CONTENTS

TABLES

ACKNOWLEDGMENTS

We thank Julia L. Armstrong for secretarial assistance; Nancy A. Bushby, Joyce E. Haber, and Lynda J. Garrett for information retrieval; Robert J. Chinnis, Stephen C. Grebe, Matthew C. Perry, Joseph B. Hunn, and Lowell C. McEwen for reviewing the manuscript; and Paul H. Eschmeyer and James R. Zuboy for editorial services.

INTRODUCTION

Chlorpyrifos (phosphorothioic acid O, O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester), also known commonly as Dursban and Lorsban, was first registered as a broad spectrum insecticide in 1965, and subsequently was used widely to control a variety of pests such as fire ants, turf and ornamental plant insects, cockroaches, mosquitos, termites, hornflies, lice, and fleas (EPA 1986). In 1982, total agricultural use of chlorpyrifos was estimated at 2.2 to 3.2 million kg, and industrial uses ranged between 0.68 and 1.04 million kg (EPA 1982). In 1984, about 0.15 million kg (0.33 million pounds) of chlorpyrifos was applied to about 600,000 ha (1.48 million acres) of wetlands in the United States for mosquito control (Odenkirchen 1987). Treatment programs in which chlorpyrifos concentrations suitable for mosquito control and other insect pests were used have been shown to be detrimental to nontarget species, including aquatic organisms, waterfowl, and terrestrial organisms from surrounding ecosystems (Linn 1968; Hurlbert et al. 1970, 1972; Atkins 1972; Streu and Cruz 1972; Nelson and Evans 1973; Butcher et al. 1977; Thirugnanam and Forgash 1977; Tagatz et al. 1982; Goodman et al. 1985a; McEwen et al. 1986; Mayer 1987; Odenkirchen 1987; Smith 1987). Domestic use of chlorpyrifos has resulted in the death of an 11-day-old infant (CDC 1980) and the poisoning of office workers (Hodgson et al. 1986). Prophylactic use of chlorpyrifos on farm animals has caused reproductive impairment of livestock (Everett 1982). Chlorpyrifos-resistant strains of insects have been detected recently; they include the German cockroach (*Blattella germanica*) in Florida and Nebraska (Milio et al. 1987) and the sawtoothed grain beetle (*Oryzaephilus surinamensis*) in Australia (Collins 1985).

This report was prepared in response to requests for information from environmental specialists of the U.S. Fish and Wildlife Service. It is part of a continuing series of brief reviews on chemical contaminants and natural resources.

ENVIRONMENTAL CHEMISTRY

Formulations of chlorpyrifos include emulsifiable concentrates, wettable powders, granules, pellets, microencapsulates and impregnated materials. Suggested diluents for concentrates include water and petroleum distillates, such as kerosene and diesel oil. Carrier compounds include synthetic clays with alkyl/aryl sulfonates as wetting agents (Table 1). Little information is available to assess the influence of various use formulations on toxicity, dispersal, decomposition, and bioavailability. Chemical and other properties of chlorpyrifos are summarized in Table 2.

The degradation half-life time ($Tb\frac{1}{2}$) of chlorpyrifos is 7.1 days in seawater (Schimmel et al. 1983), and 53 days in distilled water (Freed et al. 1979). Degradation is usually through hydrolysis to produce 3,5,6-trichloro-2-pyridinol, and phosphorthioic acid (Brust 1966; Smith 1966, 1968; Marshall and Roberts 1978). Temperature, pH, radiation, and metal cations all significantly affect chlorpyrifos $Tb\frac{1}{2}$ in water: half-life is decreased with increasing water pH, temperature, sunlight, and metal cation concentrations (Brust 1966; Mortland and Raman 1967; Smith 1968; Schaefer and Dupras 1969, 1970; Meikle and Youngson 1970).

In soil, $Tb\frac{1}{2}$ values for chlorpyrifos range from less than 1 week to more than 24 weeks, depending on soil moisture, microbial activity, clay and organic content, and temperature. In all soils studied, increasing temperature resulted in decreased $Tb\frac{1}{2}$ values (Miles et al. 1983). Degradation was more rapid in sandy loam than in organic muck soils, more rapid in moist than in dry soils, and more rapid in clay than in other soil types (Getzin 1981; Miles et al. 1983, 1984). The major routes of chlorpyrifos loss from soils are chemical hydrolysis in moist soils, clay-catalyzed hydrolysis in dry soils, and microbial degradation and volatilization (Marshall and Roberts 1978).

The half-life of chlorpyrifos in sediments is comparatively long; it was 24 days in a sediment-water slurry (Schimmel et al. 1983). In a pond treated with chlorpyrifos, total waterborne residues decreased by a factor of more than 10X, while total sediment residues rose by about 3X (Hurlbert et al. 1970). Similar results were noted in an artificial lake treated with chlorpyrifos: lake water concentrations peaked 1 day after treatment at 0.9 ug/l and plateaued near 0.2 ug/l after 3 weeks (Mulla et al. 1973).

Table 1. Selected chlorpyrifos formulations and carriers (modified from Marshall and Roberts 1978).

Compound[a]	Formulation	Carrier
Dursban 2E	Emulsifiable concentrate of 0.285 kg/l (2.4 lb/gal)	Solution in aromatic distillate with anionic/ nonionic emulsifier blend and residual chlorinated solvent
Dursban M	Emulsifiable concentrate of 0.57 kg/l (4.8 lb/gal)	As above
Dursban 6	Solution of 0.855 kg/l (7.2 lb/gal)	Solution in an aromatic distillate
Dursban $2\frac{1}{2}$G	Granular, 2.5%	Absorbed onto stabilized clay with release agents added
Lorsban 4C	Emulsifiable concentrate of 0.479 kg/l (4.0 lb/gal)	Solution in aromatic naphtha with emulsifiers
Lorsban 25W	Wettable powder, 25%.	Dispersion on blended clays with alkyl/aryl sulfonates as wetting agents

[a]Dursban and Lorsban are registered trademarks of the Dow Chemical Company.

Table 2. Chemical and other properties of chlorpyrifos (from Brust 1966; Rigterink and Kenaga 1966; Kenaga 1971; Windholz 1976).

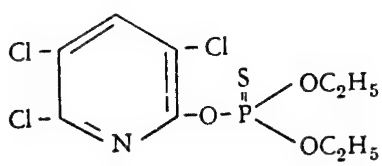
Variable	Datum
Chemical name	Phosphorothioic acid O, O-diethyl O-(3,5,6 -trichloro-2-pyridinyl) ester
Alternate names	CAS 2921-88-2; Dursban; Lorsban; Dowco 179; ENT 27311; Trichlorpyrphos; Brodan; Eradex; Killmaster; Pyrinex; Chlorpyriphos-ethyl
Primary uses	Insecticide, acaricide
Producers	Dow Chemical Company; Makhteshim-Agan (Israel); All India Medical Corp.; Planters Products, Inc.
Empirical formula	$C_9H_{11}Cl_3NO_3PS$
Structural formula	
Molecular weight	350.57
Physical state at 25 °C	White granular crystalline solid

Table 2. (concluded)

Variable	Datum
Melting point	41.5 to 43.5 °C
Vapor pressure	
25 °C	1.87×10^{-5} mm Hg
35 °C	8.87×10^{-5} mm Hg
Heat of subli-mation	26,800 cal/mol
Percent by weight	
Carbon	30.83
Hydrogen	3.16
Chlorine	30.34
Nitrogen	4.00
Oxygen	13.69
Phosphorus	8.83
Sulfur	9.15
Solubility	
Water, 23 to 25 °C	0.4-2.0 mg/l
Isooctane, 23 °C	790.0 g/kg
Methanol, 23 °C	450.0 g/kg
Log n-octanol/water partition coefficient	5.2
Soil organic carbon/ water partition co-efficient	13,600

LABORATORY INVESTIGATIONS

AQUATIC ORGANISMS

During 96-hour toxicity tests, several species of freshwater and marine invertebrates and fishes died at chlorpyrifos concentrations between 0.035 and 0.58 ug/l. LC-50 (96-hour) values, in ug chlorpyrifos/l, for sensitive species tested were 0.035 for mysid shrimp, Mysidopsis bahia; 0.11 for amphipod, Gammarus lacustris; 0.13 for fathead minnow, Pimephales promelas; 0.38 for stonefly, Pteronarcella badia; and 0.58 for striped bass, Morone saxatilis; (Mayer and Ellersieck 1986; Table 3). Toxicity was usually greater at elevated temperatures and at increasing pH levels (Johnson and Finley 1980). In general, arthropods were the most sensitive group assayed and molluscs the most tolerant (Borthwick and Walsh 1981; Table 3). The bullfrog (Rana catesbeiana) also appears to be comparatively tolerant to chlorpyrifos, as judged by a single oral LD-50 value of >400 mg/kg body weight (Hudson et al. 1984).

Sublethal effects of chlorpyrifos exposure have been documented for many species of freshwater and marine fauna; they include inhibition of cholinesterase (ChE) activity levels in brain and hematopoietic organs, sluggishness, motor incoordination, delayed maturation and growth, reproductive impairment, and reduced feed intake (Rongsriyan et al. 1968; Thirugnanam and Forgash 1977; Marshall and Roberts 1978; Tagatz et al. 1982; Jarvinen et al. 1983; EPA 1985,1986; Goodman et al. 1985b; Norberg and Mount 1985; Hansen et al. 1986). Reproductive impairment, for example, was observed in Daphnia magna at 0.08 ug chlorpyrifos/l (EPA 1985). Reduction in setting rate was shown in oyster larvae after exposure to 0.1 ug/l for 8 days (Tagatz et al. 1982). In fathead minnows exposed to 0.12 ug chlorpyrifos/l for 200 days, ChE activity was significantly reduced, fecundity was reduced, maturation delayed and, in second generation fish, growth and maturation were reduced (Jarvinen et al. 1983). Equilibrium loss was documented in 50% of brown shrimp (Penaeus aztecus) after exposure to 0.32 ug chlorpyrifos/l for 24 hours (Marshall and Roberts 1978). Growth of the California grunion (Leuresthes tenuis) was reduced 20% in an early life stage during immersion in 0.5 ug chlorpyrifos/l for 35 days and 26% in fry after exposure to 1.0 ug/l for 26 days (Goodman et al. 1985b). Additional and more comprehensive data on sublethal effects of chlorpyrifos to aquatic biota are listed elsewhere (EPA 1986).

Table 3. Acute toxicities of chlorpyrifos to selected species of aquatic invertebrates and fishes. Values are in ug chlorpyrifos per liter of medium fatal to 50 percent in 96 hours.

Organism, and other variables	LC-50, in ug/l	Reference[a]
INVERTEBRATES		
Mysid, *Mysidopsis bahia*	0.035	1
Dragonfly (naiad), *Pseudagrion* spp.	0.10[b]	2
Amphipod, *Gammarus lacustris*	0.11	3
Stonefly, *Pteronarcella badia*	0.38	4
Stonefly, *Claassenia sabulosa*	0.57	4
Cladoceran, *Daphnia magna*	1.0[c]	5
Grass shrimp, *Palaemonetes pugio*	1.5[d]	5
Crayfish, *Orconectes immunis*	6.0	6
Dragonfly (naiad), *Crocothemis erythryaea*	6.0[b]	2
Stonefly (larva), *Pteronarcys californica*	10.0	4
Red crayfish, *Procambarus clarki*	41.0[e]	7
Ram's horn snail, *Helisoma trivolvis*	>2,000[f]	8
Snail, *Lanistes carinatus*	2,710[b]	2
FISH		
Fathead minnow, *Pimephales promelas*	0.13	9
Striped bass, *Morone saxatilis*	0.58	10

Table 3. (Continued)

Organism, and other variables	LC-50, in ug/l	Reference[a]
Tidewater silverside, <u>Menidia</u> <u>peninsula</u>		
Flow-through test	0.7	11
Static test	3.0	11
California grunion, <u>Leuresthes</u> <u>tenuis</u>		
Flow-through test	1.1	11
Static test	3.1	11
Atlantic silverside, <u>Menidia</u> <u>menidia</u>		
Flow-through test	1.4	11
Static test	3.4	11
Bluegill, <u>Lepomis</u> <u>macrochirus</u>		
13 °C	5.1	12
29 °C	1.1	12
Longnose killifish, <u>Fundulus</u> <u>similis</u>	4.1	1
Inland silverside, <u>Menidia</u> <u>beryllina</u>	4.2	13
Striped mullet, <u>Mugil</u> <u>cephalus</u>	5.4	1
Rainbow trout, <u>Salmo</u> <u>gairdneri</u>		
17.3 °C	9.0	6
12.7 °C	7.1	14
7.2 °C	15.0	14
1.6 °C	51.0	14
Cutthroat trout, <u>Salmo</u> <u>clarki</u>	18.0	12

Table 3. (Concluded)

Organism, and other variables	LC-50, in ug/l	Reference[a]
Lake trout, *Salvelinus namaycush*	98	12
Sheepshead minnow, *Cyprinodon variegatus*	136	13
Channel catfish, *Ictalurus punctatus*	280	12
Mosquitofish, *Gambusia affinis*	340[b]	2
Gulf toadfish, *Opsanus beta*	520	13

[a]References: 1, Schimmel et al. 1983; 2, Karim et al. 1985; 3, Sanders 1969; 4, Sanders and Cope 1968; 5, Marshall and Roberts 1978; 6, Phipps and Holcombe 1985; 7, Chang and Lange 1967; 8, Kenaga et al. 1965; 9, Jarvinen and Tanner 1982; 10, Korn and Earnest 1974; 11, Borthwick et al. 1985; 12, Johnson and Finley 1980; 13, Clark et al. 1985; 14, Macek et al. 1969.

[b]24-hour LC-50.

[c]6.6-hour LC-50.

[d]48-hour LC-50.

[e]36-hour LC-50.

[f]72-hour LC-50.

Bioconcentration of chlorpyrifos from the medium varied substantially among five species of fishes, but generally paralleled ambient levels of chlorpyrifos (Table 4). Increases in bioconcentration factors (BCF) in chlorpyrifos-exposed teleosts may be associated with three variables: increased metabolic rate, as indicated by hyperventilation, hyperactivity, and decreased growth; increased bioavailability of chlorpyrifos as a result of solvent-induced supersaturation or increased food availability; and decreased depuration rates due to possible physiological dysfunction (Goodman et al. 1985a, b; Hansen et al. 1986). At high BCFs, adverse effects on growth and survival were observed in sheepshead minnow (Cyprinodon variegatus) by Cripe et al. (1986) and in Gulf toadfish (Opsanus beta) by Hansen et al. (1986). Chlorpyrifos is excreted rapidly from fish; the estimated $Tb\frac{1}{2}$ is 8.7 hours, and equilibration occurs with the surrounding medium in 24 to 72 hours (Smith et al. 1966; Blau and Neely 1975; Marshall and Roberts 1978). No detectable chlorpyrifos residues were found after 12 days in 10 species of estuarine invertebrates--including oligochaete annelids, molluscs, and crustaceans--after treatment with 0.046 kg chlorpyrifos/ha (Marganian and Wall 1972).

BIRDS AND MAMMALS

Signs of chlorpyrifos intoxication, as summarized by Hudson et al. (1984), include excessive blinking, hypoactivity, hyperexcitability, excessive drinking, muscular incoordination, rapid breathing, muscular weakness, tremors, piloerection (mammals) or fluffed feathers (birds), salivation, lacrimation, diarrhea, excessive urination, prostration, loss of righting reflex, spasms, tetany, coma, and convulsions. Death usually occurs between 1 hour and 9 days after exposure. Chlorpyrifos oxon (0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl) phosphate) is the active oxygen analog of chlorpyrifos and is probably responsible for most of the anticholinesterase mode of action of chlorpyrifos; the oxon is extensively and rapidly detoxified in mammalian liver via enzymatic hydrolysis by at least two microsomal esterases (Sultatos and Murphy 1983). Significant accumulations of chlorpyrifos were not detected in domestic turkeys (Meleagris gallopavo) and chickens. In birds kept in pens on soil treated with 4.5 to 9.0 kg active ingredients chlorpyrifos/ha, tissue residues were 0.16 mg/kg after 1 week; these decreased thereafter, although birds remained on the treated soil (Kenaga 1974).

LD-50 values, based on a single oral dose, ranged from 5 to 157 mg chlorpyrifos/kg body weight (BW) in birds, and from 151 to 1,000 in mammals; however, 7 of 14 avian species had reported LD-50 values of <25.0 mg/kg BW (Table 5). Many species of birds that survived chlorpyrifos poisoning showed gross pathological changes (Tucker and Crabtree 1970); furthermore, the slope of the acute dose-response curve was low (Hudson et al. 1984). These findings suggested that decreasing dosage levels did not produce proportional decreases in response, and indicated a reduced safety margin for chlorpyrifos owing to mortalities that occur frequently at levels much lower than the calculated LD-50 values (Hudson et al. 1984); however, more research is needed to verify this trend.

Table 4. Chlorpyrifos bioconcentration factors (BCF) by selected species of fishes (Goodman et al. 1985a,b; Hansen et al. 1986).

Species	Exposure duration, in days	Mean concentration in medium, in ug/l	Approximate BCF[a]
Gulf toadfish, *Opsanus beta*	49	1.4	100
	49	3.7	260
	49	8.2	270
	49	9.7	480
	49	24.0	620
	49	46.0	650
California grunion, *Leuresthes tenuis*	35	0.14	1,000
	35	0.30	700
	35	0.63	620
	26	0.13	<1
	26	0.28	58
	26	0.62	66
	26	1.3	450
Inland silverside, *Menidia beryllina*	28	0.08	<1
	28	0.18	105
	28	0.36	200
	28	0.75	130
	28	1.8	440
Atlantic silverside, *Menidia menidia*	28	0.08-1.1	<1
Tidewater silverside, *Menidia peninsulae*	28	0.09	410
	28	0.19	400
	28	0.38	580

[a] Bioconcentration factor: concentration in whole organism (ug/kg fresh weight) divided by concentration in medium (ug/l).

Reduction in cholinesterase activity levels of various tissues (blood, brain) is one of the earliest signs of chlorpyrifos intoxication. Cholinesterase reductions have been demonstrated in turkeys fed diets containing 50 mg chlorpyrifos/kg (estimated daily dose of 0.7 mg/kg BW) for 20 days (Schlinke et al. 1969), in chickens fed diets of 25 mg/kg (estimated daily dose of 0.94 mg/kg BW) for 20 days (Schlinke 1970), and in mallard (Anas platyrhynchos) ducklings fed 75 mg chlorpyrifos/kg diet for 14 days (Herin et al. 1978). Low temperatures (27.5 ^{o}C vs. 35 ^{o}C) potentiated dose-related ChE depression in juvenile nothern bobwhite (Colinus virginianus), suggesting a need for more research on cold stress interactions between acute oral chlorpyrifos exposure (Maguire and Williams 1987).

Dietary concentrations of 30 to 100 mg chlorpyrifos/kg feed produce some deaths in birds, and 136 to about 500 mg/kg feed usually kills at least 50% (Table 6). In chickens fed diets of 100 mg chlorpyrifos/kg--equivalent to an estimated daily dose of 6.8 mg/kg BW--egg fertility was reduced by 15% and hatchability by 17% (Schom et al. 1973). Dietary levels lethal to mallard ducklings were 136 to 180 mg/kg feed, equivalent to 10 mg/kg BW fed daily for 5 days (Kenaga 1974). In adult mallards given diets containing 80 mg chlorpyrifos/kg for 60 to 84 days, body weight, food consumption, brain cholinesterase actvity levels, and egg production were all reduced; moreover, egg weight and eggshell thickness were reduced, the resultant ducklings weighed less than controls, and survival was comparatively poor at age 7 days. No effect on any variable was observed at diets of 8 mg/kg (Gile and Meyers 1986; Meyers and Gile 1986).

Dermal application routes are also toxic. Some deaths were recorded in turkeys from dermal treatments of 15 to 20 mg chlorpyrifos/kg BW (Schlinke et al. 1969). Higher levels applied to feathers killed turkeys within 8 hours (Marshall and Roberts 1978). Newborn piglets (Sus spp.) were especially more sensitive than those 30-36 hours old to cutaneous applications of chlorpyrifos; newborns showed clinical signs consistent with organophosphorus toxicosis after a 2.5% aerosol preparation (dosage unknown) was applied to the tail and umbilicus (Long et al. 1986). Accidental poisoning of cattle (Bos spp.) by chlorpyrifos through dermal application to control ticks resulted in some deaths; among bulls that survived, sperm production was reduced 43% in seriously affected animals and 12% in those with no outward signs of poisoning (Everett 1982).

Chlorpyrifos is not mutagenic, as judged by mitotic recombination assays (Poole et al. 1976), and did not increase sister chromatid exchange above background in tests with chick (Gallus spp.) embryos and Chinese hamster (Cricetus spp.) ovary cells (Muscarella et al. 1984).

Table 5. Chlorpyrifos toxicity to a variety of birds and mammals via single oral dose route of administration. Values are in mg chlorpyrifos/kg body weight lethal to 50% within 14 days.

Organism, and other variables	LD-50, in mg/kg body weight	Reference[a]
BIRDS		
European starling, <u>Sturnus vulgaris</u>	5	1
Ring-necked pheasant, <u>Phasianus colchicus</u>		
Male	8.4	2
Female	17.7	3
Red-winged blackbird, <u>Agelaius phoeniceus</u>	13	1
Common grackle, <u>Quiscalus quiscula</u>	13	1
House sparrow, <u>Passer domesticus</u>	10 to 21	1,3
Japanese quail, <u>Coturnix japonica</u>	15.9	2
Sandhill crane, <u>Grus canadensis</u>	25 to 50	3
Rock dove, <u>Columba livia</u>	26.9	2
Crow, <u>Corvus brachyrhynchos</u>	>32	1
Canada goose, <u>Branta canadensis</u>	40 to 80	4
Chukar, <u>Alectoris chukar</u>		
Male	61.1	3
Female	60.7	2

Table 5. (Concluded)

Organism, and other variables	LD-50, in mg/kg body weight	Reference[a]
Northern bobwhite, *Colinus virginianus*		
Technical grade	32	5
Lorsban 15G	108	5
Mallard, *Anas platyrhynchos*		
Age 36 hours	14.5	6
Age 7 days	29.4	6
Age 30 days	50.4	6
Age 6 months	83.3	6
Ringed turtle dove, *Streptopelia risoria*	157	5
MAMMALS		
Albino rat, *Rattus norvegicus*	151	4
Guinea pig, *Cavia porcellus*	500	7
Domestic goat, *Capra hircus*	500 to 1,000	4
White rabbit, *Oryctolagus cuniculus*	1,000 to 2,000	7

[a]References: 1, Schafer 1972; 2, Tucker and Haegele 1971; 3, Tucker and Crabtree 1970; 4, Hudson et al. 1984; 5, Hill and Camardese 1984; 6, Hudson et al. 1972; 7, Smith 1987.

Table 6. Dietary toxicity of chlorpyrifos to selected species of birds.

Species, and age (in days)	Duration of dietary exposure, in days	Minimum lethal concentration, in mg/kg diet	LD-50, in mg/kg diet	Reference
Mallard, Anas platyrhynchos				
(1 to 5)	5	30	136	1
(5 to 7)	5	30 to 90	180	1
(10)	5 plus 3 untreated	-	940	2
Pekin duck, Anas sp.				
(5)	21	-	>1,000	1
Northern bobwhite, Colinus virginianus				
(1 to 5)	5	50 to 100	505	1
Turkey, Meleagris gallopavo				
(84)	28	>100	>100	1
Japanese quail, Coturnix japonica				
(14)	5 plus 3 untreated	-	299	2
(14)	5 plus 3 untreated	-	492	3
Chicken, Gallus sp.				
(10 to 12)	14	<200	400	1
(28)	28	50 to 100	>100	1
(Adults)	365	-	>200	1
Ring-necked pheasant, Phasianus colchicus				
(10)	5 plus 3 untreated	-	553	2
Coturnix quail, Coturnix risoria				
(14 to 21)	5	-	299	1
(Adults)	28	300	500	1

[a]References: 1, Kenaga, 1974; 2, Hill et al. 1975; 3, Hill and Camardese 1986.

Chlorpyrifos-impregnated ear tags are under development to control horn flies (Haematobia irritans) in U.S. cattle (Byford et al. 1986). Cattle fitted with ear tags (0.96 g chlorpyrifos per tag/365 kg animal, or about 2.6 mg chlorpyrifos/kg BW) had slightly elevated tissue residues (0.13 mg/kg fat) after 12 weeks, but residues were well within current acceptable tolerance levels of 2.0 mg chlorpyrifos/kg fresh weight cattle fat, meat, or meat by-products (Byford et al. 1986). In dogs (Canis familiaris), chlorpyrifos-impregnated collars provided effective control of adult fleas (Ctenocephalides spp.) for up to 11 months, with no significant adverse reactions regardless of canine coat length, size, or age (Higgins and Jarvis 1986).

FIELD INVESTIGATIONS

There have been many accidental spills of chlorpyrifos, but little quantitative assessment of the environmental effects. One exception is a spill in April 1985 in England (Boreham and Birch 1987). In that instance, a truck overturned, spilling 205 liters of chlorpyrifos into an adjacent stream that drained into the Roding River. A resulting sharp decrease in the number and type of macroinvertebrate benthic organisms in affected parts of the river, compared to unaffected areas, lasted 6 months. In addition, certain chlorpyrifos-resistant benthic organisms were unusually abundant.

Chlorpyrifos controls mosquito larvae at applied dosages between 0.028 and 0.056 kg/ha, equivalent to 9 to 18 ug chlorpyrifos/l in 152 mm (6 inches) of water (Marshall and Roberts 1977; Eaton et al. 1985); in 1984 alone, chlorpyrifos was used for this purpose on about 600,000 ha (Odenkirchen 1987). No obvious deleterious effects of chlorpyrifos have yet been noted in mammals, amphibians, or reptiles under field conditions of current use (Table 7). However, at recommended dosage application rates for control of mosquitos and other pestiferous insects (usually 0.028 to 0.056 kg/ha), adverse effects have been documented on survival, reproduction, metabolism, and species diversity of a variety of fishes, terrestrial and aquatic invertebrates, freshwater flora, waterfowl, and horned larks (*Eremophila alpestris*), and on the marketability of various crops (Mulla et al. 1971, 1973; Hurlbert et al. 1972; Macek et al. 1972; Nelson and Evans 1973; Hoy and Shea 1981; Table 7).

We emphasize that the effectiveness of chlorpyrifos under field conditions, like that of other organophosphorus pesticides, is significantly modified by numerous variables such as formulation, route of administration, pond substrate, dose, and water temperature (Macek et al. 1969; Bailey et al. 1970; Rawn et al. 1978; Odenkirchen 1987).

Table 7. Chlorpyrifos effects on selected ecosystems.

Ecosystem, and other information	Application rate and other variables	Effects and reference
AQUATIC		
Lake	0.004 kg/ha, emulsifiable concentrate, oil diluent single application	After 24 hours, aquatic insect populations reduced 14% to 40% and snails reduced 10% (Moore and Breeland 1967).
Freshwater lake	0.014 kg/ha (equivalent to about 1.2 ug/l), single application	Freshwater algae (*Ankistrodesmus* sp., *Tetraedron* sp.) reduced 30% to 90% 7 days posttreatment; reduced population growth evident one year postapplication (Brown et al. 1976).
Flooded rice field	Individual applications of 0.014 to 0.019 kg/ha, emulsifiable concentrate, oil diluent, 3 applications at 5-week intervals	Mortality after 72 hours, 32% in caged bluegills (*Lepomis macrochirus*), 50% to 70% in mayfly nymphs (*Siphlonurus* sp.), and 32% in predatory diving beetles (Washino et al. 1972).
Freshwater ponds, (8 m X 17 m X 0.3 m deep)	Individual applications of 0.011, 0.056, 0.11, or 1.11 kg/ha; 4 applications at 2-week intervals	Initial population inhibition of mosquitofish (*Gambusia* sp.), but reproduction resumed except for 1.11 kg/ha group. Fish whole body residues in 0.056 kg/ha group, in mg/kg body weight, were 2.8 at 4 hours, 1.7 at 24 hours, and 0.1 after 2 weeks. Insect and zooplankton populations reduced

Table 7. (Continued)

Ecosystem, and other information	Application rate and other variables	Effects and reference
		>92%; little recovery was evident after third treatment. The 0.056 kg/ha treatment regimen, at 4 hours, resulted in residues of 10 ug/l in water, 375 ug/kg in vegetation, and nondetectable levels in mud; at 14 days, all residues were nondetectable (Hurlbert et al. 1970).
Artificial lake	0.02 kg/ha, granular formulation, single application	Chironomid larvae population remained >90% depressed for 5 months (Mulla et al. 1971).
Salt marsh	0.028 kg/ha (0.025 lbs/acre), single aerial application, mosquito larvicide granules	No observable effects on caged blue crabs (<u>Callinectes</u> <u>sapidus</u>), penaeid shrimp, or fishes; some fiddler crabs (<u>Uca</u> sp.) dead (FWS 1968).
Salt marsh	Individual applications of 0.028 kg/ha, 4 applications at 2-week intervals	In killifish (<u>Fundulus heteroclitus</u>), convulsions, ChE depression, and deaths noted. ChE remained depressed for about 10 weeks after final application (Thirugnanum and Forgash 1977).
Artificial streams, each 520 m long, 0.14 ha of surface area, with pools	Continuous treatment stream received 0.22 ug chlorpyrifos/l for days 1 to 41, and 1.0 ug/l from	When compared to control stream, no effect on total abundance of benthic organisms. How-

Table 7. (Continued)

Ecosystem, and other information	Application rate and other variables	Effects and reference
30.5 m long X 3.6 m wide X 81 cm deep	days 41 to 100. Intermittent treatment stream received dosage 14X higher than continuous treatment stream, but dosage was confined to 24 hours every 14 days. Chlorpyrifos administered as emulsifiable concentrate in petroleum derivative solvent	ever, in both treated streams, species diversity decreased by equal amounts and was still decreasing at day 100. Adverse sublethal effects were noted in fathead minnows, Pimephales promelas (spinal deformities) and bluegills (ChE inhibition, signs of organophosphorus poisoning) only in the pulse-dosed stream. In all streams, however, fish survived, grew, and reproduced equally well (Eaton et al. 1985).
Shallow pond, mean depth 0.25 m, surface area 0.11 ha, high vegetation	Individual applications of 0.056 kg/ha, technical grade, 2 applications at 34-day interval	After 63 days, 46% to 55% mortality in centrarchid populations, and 75% reduction in insect populations of caddisflies, mayflies, and midges (Macek et al. 1972).
Shallow ponds	0.056 kg/ha, emulsifiable concentrate, oil diluent single application	All caged green sunfish (Lepomis cyanellus) died (Linn 1968).
Woodland pools	Single application of 0.056 kg/ha, granular formulation	Increased algal growth on leaf litter observed months after treatment, attributed to reduction in grazing stress by mosquito larvae (Hagmann and Porteous 1972).
Woodland pools	0.056 kg/ha, granular formulation, single application	Isopod populations reduced 90% to 95% (Cooney and Pickard 1974).

Table 7. (Continued)

Ecosystem, and other information	Application rate and other variables	Effects and reference
Freshwater ponds	Single dose of chlorpyrifos, equivalent to 4, 10, or 1,000 ug/l.	Increased algal bloom duration in treated ponds, possibly due to loss of grazing fauna (Butcher et al. 1977).
Salt marsh, 202 ha (500 acres), Florida	0.56 kg/ha (0.5 lbs/acre), single application applied as aerial spray, to kill mosquito larvae	Killed significant numbers of fishes and crustaceans (FWS 1968).
Salt marsh, 78 ha plot	0.56 kg/ha, emulsifiable concentrate, once, aerially	After 48 hours, mortality was 35% in caged fish and 84% in caged shrimp; no other adverse effects were noted during the next 27 days (Wall and Marganian 1971).
Salt marsh estuary, Bay St. Louis, Mississippi, 408 ha site (1,008 acres)	0.56 kg/ha (0.5 lbs/acre), granular, single aerial application, for mosquito control	After spraying, all caged fiddler crabs died, white shrimp (<u>Penaeus setiferus</u>) populations were reduced, and large numbers of blue crabs were found dead. No observable effects on terrestrial organisms, including insects. One month after spraying, shrimp and blue crab populations seemed normal, although fiddler crabs were absent (FWS 1967).
Freshwater pond	Single application of pelletized 10.6% chlorpyrifos to obtain theoretical water concentrations of 250 ug/l and higher	Species diversity of diatoms reduced >50% in 6 weeks, vs. 12% increase in controls (Nelson et al. 1976).

Table 7. (Continued)

Ecosystem, and other information	Application rate and other variables	Effects and reference
TERRESTRIAL		
Temporary woodland pool	Average maximum water concentration of 1.6 ug chlorpyrifos/l	No obvious adverse effects on wildlife, i.e., 3 spp. of rodents, one sp. frog, one sp. turtle (Nelson and Evans 1973).
Freshwater ponds (8 m X 17 m X 0.3 m deep)	Individual applications of 0.011, 0.056, 0.11, and 1.11 kg/ha; 4 applications at 2-week in-intervals	High mortality (>42%) of mallard (Anas platyrhynchos) ducklings on all treated ponds, vs. none dead on control ponds (Hurlbert et al. 1970).
Salt marsh	0.025 kg/ha, single application	No gross effects on wildlife (Ludwig et al. 1968).
Rice field area	0.029 kg/ha, single application	All honeybees (Apis sp.) within 0.4 km downwind of spray area were dead; 95% were dead at 0.8 km and 89% at 1.2 km (Atkins 1972).
New Mexico ranchlands	Dust formulations of 0.48 and 1.97 kg/ha, to control wildlife flea populations	No observable deleterious effects in rodents and rabbits 3 to 4 weeks posttreatment (Miller et al. 1970).
Wheat fields	0.56 and 1.0 kg/ha, to control pale western cutworm (Agrotis orthogonia)	Horned larks (Eremophila alpestris) had brain ChE activity levels depressed 22% at 3 days posttreatment, and 8% at 16 days. No sick or dead birds found; however, no systematic searches were made for

Table 7. (Concluded)

Ecosystem, and other information	Application rate and other variables	Effects and reference
		the small lark carcasses, nor were specific observations for toxic signs conducted (McEwen et al. 1986).
Iraqi date palm (Phoenix sp.) orchards	Emulsifiable concentrate applied once after fruiting and infestation with high pressure ground sprayers at 0.98 kg/ha to control insect pests	Chlorpyrifos residues in dates decreased from 1.28 mg/kg fresh weight at day one postapplication to 0.2 mg/kg on day 15, to 0.05 on day 29, and to nondetectable concentrations on day 71. Concentrations of the chlorpyrifos oxygen analog, however, after reaching a peak of 0.5 mg/kg on day 15, were still detectable (0.1 mg/kg) at day 85, suggesting that dates should be harvested at least 8 weeks after chlorpyrifos treatment (Mansour 1985).
Turf	1.12 kg/ha, emusifiable concentrate, single application, to control chinch bug (Blissus leucopterus listus)	Most arthropods in turf killed immediately after application. Target pest populations remained depressed for one year posttreatment, but other insect populations recovered to levels greater than controls after 3.5 months (Streu and Cruz 1972).

RECOMMENDATIONS

Current water quality criteria formulated for chlorpyrifos by the U.S. Environmental Protection Agency (EPA 1986) for aquatic life protection seem to afford a reasonable degree of safety, at least during short-term exposure. Specifically, the proposed criteria for freshwater are 0.041 ug/l (4-day average concentration) and 0.083 ug/l (1-hour average concentration), neither of which should be exceeded more than once every 3 years; for saltwater, the criteria are 0.0056 ug/l and 0.011 ug/l, respectively.

The acceptable tolerance level of chlorpyrifos in meat and meat by-products destined for human consumption is 2.0 mg/kg fresh weight (Byford et al. 1986). The significance of this concentration to animal health, or to consumers other than man, is unknown. More research is needed to establish maximum tolerable chlorpyrifos limits in tissues of sensitive fish and wildlife.

Information is lacking on the effectiveness of chlorpyrifos in large-scale (>40 ha) coldwater ecosystems, typical of those found in Alaska or northern tier States; accordingly, we recommend initiation of long-term studies in these potential problem areas.

As judged by our analysis of available literature, three courses of action now seem warranted: (1) Restrict the use of chlorpyrifos for mosquito control in wetlands, estuaries, and waterfowl breeding areas because recommended treatment levels are demonstrably harmful to nontarget species, including mallard ducklings. The unsuitability of chlorpyrifos for mosquito control is further supported by the finding that certain mosquito populations in California are showing signs of chlorpyrifos resistance, and thus may require more aggressive future treatment programs (Reisen et al. 1984). (2) Curtail agricultural use of chlorpyrifos in watershed areas pending acquisition of additional data on its transport, fate, and effects, including data on chlorpyrifos flux rates from soils and sediments and its resultant bioavailability. (3) Develop suitable replacements for chlorpyrifos in mosquito control programs. These replacement compounds should exhibit a relatively long half-life in aquatic environments while avoiding the broad spectrum toxicity typical of chlorpyrifos to large numbers of nontarget organisms.

LITERATURE CITED

Atkins, E. L. 1972. Rice field mosquito control studies with low volume Dursban sprays in Colusa County, California. V. Effects on honey bees. Mosq. News 32:538-541.

Bailey, D. L., G. C. Labrecque, and T. L. Whitfield. 1970. Slow-release and emulsifiable formulations of Dursban and Abate for controlling larvae of Culex pipiens quinquefasciatus. Mosq. News 30:465-467.

Blau, G. E., and W. B. Neely. 1975. Mathematical model building with an application to determine the distribution of Dursban insecticide added to a simulated ecosystem. Adv. Ecol. Res. 9:133-162.

Boreham, S., and P. Birch. 1987. The use of indicator organisms to assess aquatic pollution following a motorway insecticide spill. Sci. Total Environ. 59:477-480.

Borthwick, P. W., J. M. Patrick, Jr., and D. P. Middaugh. 1985. Comparative acute sensitivities of early life stages of atherinid fishes to chlorpyrifos and thiobencarb. Arch. Environ. Contam. Toxicol. 14:465-473.

Borthwick, P. W., and G. E. Walsh. 1981. Initial toxicological assessment of Ambush, Bolero, Bux, Dursban, Fentrifanil, Larvin, and Pydrin: static acute toxicity tests with selected estuarine algae, invertebrates, and fish. U.S. Environ. Protection Agency Rep. 600/4-81-076. 20 pp.

Brown, J. R., L. Y. Chow, and C. B. Deng. 1976. The effects of Dursban upon fresh water phytoplankton. Bull. Environ. Contam. Toxicol. 15:437-441.

Brust, H. F. 1966. A summary of chemical and physical properties of Dursban. Down to Earth 22:21-22.

Butcher, J. E., M. G. Boyer, and C. D. Fowle. 1977. Some changes in pond chemistry and photosynthetic activity following treatment with increasing concentrations of chlorpyrifos. Bull. Environ. Contam. Toxicol. 17:752-758.

Byford, R. L., J. A. Lockwood, S. M. Smith, C. W. Harmon, C. C. Johnson, D. G. Luther, H. F. Morris, Jr., and A. J. Penny. 1986. Insecticide residues in cattle treated with a cypermethrin, chlorpyrifos, piperonyl butoxide-impregnated ear tag. Bull. Environ. Contam. Toxicol. 37:692-697.

CDC. 1980. Pesticide poisoning in an infant. Center for Disease Control, Mortal. Morbid. 29:254-255.

Chang, V. C. S., and W. H. Lange. 1967. Laboratory and field evaluation of selected pesticides for control of red crayfish in California rice fields. J. Econ. Entomol. 60:473-477.

Clark, J. R., J. M. Patrick, Jr., D. P. Middaugh, and J. C. Moore. 1985. Relative sensitivity of six estuarine fishes to carbophenothion, chlorpyrifos, and fenvalerate. Ecotoxicol. Environ. Safety 10:382-390.

Collins, P. J. 1985. Resistance to grain protectants in field populations of the sawtoothed grain beetle in southern Queensland. Aust. J. Exp. Agric. 25:683-686.

Cooney, J. C., and E. Pickard. 1974. Field tests with Abate and Dursban insecticides for control of flood water mosquitos in the Tennessee Valley region. Mosq. News 34:12-22.

Cripe, G. M., D. J. Hansen, S. F. Macauley, and J. Forester. 1986. Effects of diet quantity on sheepshead minnows (Cyprinodon variegatus) during early life-stage exposures to chlorpyrifos. Pages 450-460 in T. M. Poston and R. Purdy (eds.). Aquatic toxicology and environmental fate: ninth symposium. ASTM Spec. Tech. Publ. 921, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Eaton, J., J. Arthur, R. Hermanutz, R. Kiefer, L. Mueller, R. Anderson, R. Erickson, B. Nordlung, J. Rogers, and H. Pritchard. 1985. Biological effects of continuous and intermittent dosing of outdoor experimental streams with chlorpyrifos. Pages 85-118 in R. C. Bahner and D. J. Hansen (eds.). Aquatic toxicology and hazard assessment: eighth symposium. ASTM Spec. Tech. Publ. 891, American Society for Testing and Materials, Philadelphia, Pennsylvania.

EPA. 1982. Preliminary quantitative use analysis. Available from U.S. Environ. Protection Agency, Economics Analysis Branch, 401 M St. S.W., Washington D.C., 20460. 10 pp.

EPA. 1985. Disciplinary review ecological effects profile. Available from U.S. Environ. Protection Agency, Office of Pesticide Programs, 401 M St. S.W., Washington D.C. 20460. 10 pp.

EPA. 1986. Ambient water quality criteria for chlorpyrifos - 1986. U.S. Environ. Protection Agency Rep. 440/5-86-005. 64 pp.

Everett, R. W. 1982. Effects of Dursban 44 on semen output of Holstein bulls. Dairy Sci. 65:1781-1791.

Freed, V. H., C. T. Chiou, and D. W. Schmedding. 1979. Degradation of selected organophosphate pesticides in water and soil. J. Agric. Food Chem. 27:706.

FWS. 1967. Effects of granular application of Dursban on some estuary and salt marsh organisms. U.S. Fish. Wildl. Serv. Spec. Rep., Pesticide Surveillance Program, Atlanta, Georgia. Mimeo. 34 pp.

FWS. 1968. Field appraisal of tests to control salt marsh mosquito with Dursban applied as a larvicide and adulticide in Florida. U.S. Fish Wildl. Serv. Spec. Rep., Pesticide Field Appraisal Program, Atlanta, Georgia. Mimeo. 25 pp.

Getzin, L. W. 1981. Dissipation of chlorpyrifos from dry soil surfaces. J. Econ. Entomol. 74:707-713.

Getzin, L. W., and I. Rosenfield. 1968. Organophosphorus insecticide degradation by heat-labile substances in soil. J. Agric. Food Chem. 16: 598-601.

Gile, J. D., and S. M. Meyers. 1986. Effects of adult mallard age on avian reproductive tests. Arch. Environ. Contam. Toxicol. 15:751-756.

Goodman, L. R., D. J. Hansen, D. P. Middaugh, G. M. Cripe, and J. C. Moore. 1985a. Method for early life-stage toxicity tests using three atherinid fishes and results with chlorpyrifos. Pages 145-154 in R. D. Cardwell, R. Purdy and R. C. Bahner (eds.). Aquatic toxicology and hazard assessment: seventh symposium. ASTM Spec. Tech. Publ. 854, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Goodman, L. R., D. J. Hansen, G. M. Cripe, D. P. Middaugh, and J. C. Moore. 1985b. A new early life-stage toxicity test using the California grunion (*Leuresthes tenuis*) and results with chlorpyrifos. Ecotoxicol. Environ. Safety 10:12-21.

Hagmann, L. E., and D. J. Porteous. 1972. Pre-hatch treatments with Dursban 1G granular insecticide for control of mosquito larvae. Down to Earth 28:21-24.

Hansen, D. J., L. R. Goodman, G. M. Cripe, and S. F. Macauley. 1986. Early life-stage toxicity test methods for Gulf toadfish (Opsanus beta) and results using chlorpyrifos. Ecotoxicol. Environ. Safety 11:15-22.

Harris, C. R., H. J. Svec, and P. Martel. 1975. Laboratory and field studies on the effectiveness of post planting insecticide treatments in controlling the darksided and redbacked cutworms attacking tobacco. Proc. Entomol. Soc. Ont. 104:59-64.

Herin, R. A., J. E. Sluggs, E. M. Loves, L. T. Heiderscheit, J. D. Farmer, and D. Prather. 1978. Correlation of salt gland function with levels of chlorpyrifos in the feed of mallard ducklings. Pestic. Biochem. Physiol. 9:157-164.

Higgins, P. C., and R. A. Jarvis. 1986. Chlorpyrifos - the latest advance in controlling fleas in dogs and cats. Aust. Vet. Pract. 16:103.

Hill, E. F., and M. B. Camardese. 1984. Toxicity of anticholinesterase insecticides to birds: technical grade versus granular formulations. Ecotoxicol. Environ. Safety 8:551-563.

Hill, E. F., and M. B. Camardese. 1986. Lethal dietary toxicities of environmental contaminants and pesticides to coturnix. U.S. Fish Wildl. Serv., Fish Wildl. Tech. Rep. 2. 147 pp.

Hill, E. F., R. G. Heath, J. W. Spann, and J. D. Williams. 1975. Lethal dietary toxicities of environmental pollutants to birds. U.S. Fish Wildl. Serv. Spec. Sci. Rep.--Wildl. No. 191. 61 pp.

Hodgson, M. J., G. D. Block, and D. K. Parkinson. 1986. Organophosphate poisoning in office workers. J. Occup. Med. 28:434-437.

Hoy, J. B., and P. J. Shea. 1981. Effects of lindane, chlorpyrifos, and carbaryl on a California pine forest soil arthropod community. Environ. Entomol. 10:732-740.

Hudson, R. H., R. K. Tucker, and M. A. Haegele. 1972. Effects of age on sensitivity: acute oral toxicity of 14 pesticides to mallard ducks of several ages. Toxicol. Appl. Pharmacol. 22:556-561.

Hudson, R. H., R. K. Tucker, and M. A. Haegele. 1984. Handbook of toxicity of pesticides to wildlife. U.S. Fish Wildl. Serv. Resour. Publ. 153. 90 pp.

Hurlbert, S.H., M.S. Mulla, J.O. Keith, W.E. Westlake, and M. E. Dusch. 1970. Biological effects and persistence of Dursban® in freshwater ponds. J. Econ. Entomol. 63:43-52.

Hurlbert, S. H., M. S. Mulla, and H. R. Willson. 1972. Effects of an organophosphorus insecticide on the phytoplankton, zooplankton, and insect populations of fresh-water ponds. Ecol. Monogr. 42:269-299.

Jarvinen, A. W., B. R. Nordling, and M. E. Henry. 1983. Chronic toxicity of Dursban® (chlorpyrifos) to the fathead minnow (Pimephales promelas) and the resultant acetylcholinesterase inhibition. Ecotoxicol. Environ. Safety 7:423-434.

Jarvinen, A. W., and D. K. Tanner. 1982. Toxicity of selected controlled released and corresponding unformulated technical grade pesticides to the fathead minnow (Pimephales promelas). Environ. Pollut. 27A:179-195.

Johnson, W. W., and M. T. Finley. 1980. Handbook of acute toxicity of chemicals to fish and aquatic invertebrates. U.S. Fish Wildl. Serv. Resour. Publ. 137. 98 pp.

Karim, A.A.R.A., A.A.M. Haridi, and E.A.E. Rayah. 1985. The environmental impacts of four insecticides on non-target organisms in the Gezira irrigation scheme canals of Sudan. J. Trop. Med. Hyg. 88:161-168.

Kenaga, E. E. 1971. Some physical, chemical and insecticidal properties of some O-O-dialkyl O-(3,5,6-trichloro-2-pyridyl) phosphates and phosphorothioates. Bull. World Health Org. 44:225-228.

Kenaga, E. E. 1974. Evaluation of the safety of chlorpyrifos to birds in areas treated for insect control. Residue Rev. 50:1-41.

Kenaga, E. E., W. K. Whitney, J. L. Hardy, and A. E. Doty. 1965. Laboratory tests with Dursban® insecticide. J. Econ. Entomol. 58:1043-1050.

Korn, S., and R. Earnest. 1974. Acute toxicity of 20 insecticides to striped bass (Morone saxtilis). Calif. Fish Game 60:128-131.

Linn, J. D. 1968. effects of low volume spraying of Dursban and Fenthion on fish. Down to Earth 24:28-30.

Long, G. G., A. B. Scheidt, R. J. Everson, and F. W. Oehme. 1986. Age related susceptibility of newborn pigs to the cutaneous application of chlorpyrifos. Vet. Hum.Toxicol. 28:297-299.

Ludwig, P.D., H.J. Dishburger, J.C. McNeill, W.D. Miller and J.R. Rice. 1968. Biological effects and persistence of Dursban® insecticide in a salt-marsh habitat. J. Econ. Entomol. 61:626-633.

Macek, K. J., C. Hutchinson, and O. B. Cope. 1969. The effects of temperature on the susceptibility of bluegills and rainbow trout to selected pesticides. Bull. Environ. Contam. Toxicol. 4:174-183.

Macek, K. J., D. F. Walsh, J. W. Hogan, and D. D. Holz. 1972. Toxicity of the insecticide Dursban® to fish and aquatic invertebrates in ponds. Trans. Am. Fish. Soc. 101:420-427.

Maguire, C. C., and B. A. Williams. 1987. Cold stress and acute organophosphorus exposure: interaction effects on juvenile northern bobwhite. Arch. Environ. Contam. Toxicol. 16:477-481.

Mansour, S. A. 1985. Determination of residues of chlorpyrifos and its oxygen analog in dates. J. Pestic. Sci. 10:677-680.

Marganian, V. M., and W. J. Wall, Jr. 1972. Dursban® and diazinon residues in biota following treatment of intertidal plots on Cape Cod -- 1967-69. Pestic. Monit. J. 6:160-165.

Marshall, W. F., and J. R. Roberts. 1978. Ecotoxicology of chlorpyrifos. Natl. Res. Counc. Canada, Assoc. Comm. Sci. Crit. Environ. Qual., Publ. 16059, Ottawa, Ontario, Canada. 314 pp.

Mayer, F. L., Jr. 1987. Acute toxicity handbook of chemicals to estuarine organisms. U.S. Environ. Protection Agency Rep. 600/8-87/017. 274 pp.

Mayer, F. L., Jr., and M. R. Ellersieck. 1986. Manual of acute toxicity: interpretation and data base for 410 chemicals and 66 species of freshwater animals. U.S. Fish Wildl. Serv. Resour. Publ. 160. 579 pp.

McEwen, L. C., L. R. DeWeese, and P. Schladweiler. 1986. Bird predation on cutworms (Lepidoptera : Noctuidae) in wheat fields and chlorpyrifos effects on brain cholinesterase activity. Environ. Entomol. 15:147-151.

Meikle, B. W., and C. R. Youngson. 1970. Hydrolysis rate of Dowco 179 in water. Dow Chemical Company. Agric. Res. Rep. GS-1154. 6 pp. Walnut Grove Creek, California.

Meyers, S. M., and J. D. Gile. 1986. Mallard reproductive testing in a pond environment: a preliminary study. Arch. Environ. Contam. Toxicol. 15: 757-761.

Miles, J.R.W., C.R. Harris, and C.M. Tu. 1983. Influence of temperature on the persistence of chlorpyrifos and chlorfenvinphos in sterile and natural mineral and organic soils. J. Environ. Sci. Health B18:705-712.

Miles, J.R.W., C.R. Harris, and C.M. Tu. 1984. Influence of moisture in the persistence of chlorpyrifos and chlorfenvinphos in sterile and natural mineral and organic soils. J. Environ. Sci. Health B19:237-243.

Milio, J. F., P. G. Koehler, and R. S. Patterson. 1987. Evaluation of three methods for detecting chlorpyrifos resistance in German cockroach (Orthoptera: Blattellidae) populations. J. Econ. Entomol. 30:44-46.

Miller, B.E., D.L. Forcum, K.W. Week, J.R. Wheeler, and C.D. Rail. 1970. An evaluation of insecticides for flea control on wild animals. J. Med. Entomol. 7:697-702.

Moore, J. B., and S. G. Breeland. 1967. Field evaluation of two mosquito larvicides, Abate and Dursban against Anopheles quadrimaculatus and associated Culex species. Mosq. News 27:105-111.

Mortland, M. M., and K. U. Raman. 1967. Catalytic hydrolysis of some organic phosphate pesticides by copper (II). Agric. Food Chem. 15:163-167.

Mulla, M. S., R. L. Norland, and D. M. Fanuva. 1971. Control of chironomid midges in recreational lakes. J. Econ. Entomol. 64:300-307.

Mulla, M. S., R. L. Norland, W. E. Westlake, B. Dell, and J. S. Amant. 1973. Aquatic midge larvicides: their efficacy and residues in water, soil, and fish in a warm water lake. Environ. Entomol. 2:58-65.

Muscarella, D. E., J. F. Keown, and S. E. Bloom. 1984. Evaluation of the genotoxic and embroyotoxic potential of chlorpyrifos and its metabolites in vivo and in vitro. Environ. Mut. 6:13-23.

Nelson, J. H., and E. S. Evans, Jr. 1973. Field evaluations of the larvicidal effectiveness. Effects on non-target species and environmental residues of a slow-release polymer formulation of chlorpyrifos. U.S. Army Environ. Hygiene Agency Rep. No. 44-022-73/75. Aberdeen Proving Ground, Maryland. 15 pp.

Nelson, J. H., D. L. Stoneburner, E. S. Evans, Jr., N. E. Pennington, and M. V. Meisch. 1976. Diatom diversity as a function of insecticidal treatment with a controlled-release formulation of chlorpyrifos. Bull. Environ. Contam. Toxicol. 15:630-634.

Norberg, T. J., and D. I. Mount. 1985. A new fathead minnow (Pimephales promelas) subchronic toxicity test. Environ. Toxicol. Chem. 4:711-718.

Odenkirchen, E. W. 1987. Hazards of chlorpyrifos, an organophosphorus pesticide, to natural resources: a review. M.A. Thesis. The American University, Washington, D.C. 63 pp.

Phipps, G. L., and G.W. Holcombe. 1985. A method for aquatic multiple species toxicant testing: acute toxicity of 10 chemicals to 5 vertebrates and 2 invertebrates. Environ. Pollut. 38A:141-157.

Poole, D.C., V.F. Simmon, and G.W. Newell. 1976. In vitro mutagenic activity of fourteen pesticides. Toxicol. Appl. Pharmacol. 41:196.

Rawn, G. P., G. R. B. Webster, and G. M. Findlay. 1978. Effect of pool bottom substrate on residues and bioactivity of chlorpyrifos, against larvae of Culex tarsalis (Diptera: Culicidae). Can. Entomol. 110:1269-1276.

Reisen, W.K., G. Yoshimura, W.C. Reeves, M.M. Milby, and R.P. Meyer. 1984. The impact of aerial applications of ultra-low volume adulticides on Culex tarsalis populations (Diptera: Culicidae) in Kern County, California, USA, 1982. J. Med. Entomol. 21:573-585.

Rigterink, R. H., and E. E. Kenaga. 1966. Synthesis and insecticidal activity of some 0,0-dialkyl 0-3,5,6-trichloro-2-pyridyl phosphates and phosphorothioates. J. Agric. Food Chem. 14:304-306.

Rongsriyam, Y., S. Prownebon, and S. Hirakoso. 1968. Effects of insecticides on the feeding activity of the guppy, a mosquito eating fish, in Thailand. Bull. World Health Org. 39:977-980.

Sanders, H. O. 1969. Toxicity of pesticides to the crustacean Gammarus lacustris. U.S. Fish Wildl. Serv. Tech. Paper 25. 14 pp.

Sanders, H. O., and O. B. Cope. 1968. The relative toxicity of several pesticides to naiads of three species of stoneflies. Limnol. Oceanog. 13: 112-117.

Schaefer, C.H., and E.F. Dupras, Jr. 1969. The effects of water quality, temperature and light on the stability of organophosphorus larvicide used for mosquito control. Proc. Pap. Annu. Conf. Calif. Mosq. Control Assoc. 37:67-75.

Schaefer, C. H., and E. F. Dupras, Jr. 1970. Factors affecting the stability of Dursban in polluted waters. J. Econ. Entomol. 63:701-705.

Schafer, E. W. 1972. The acute oral toxicity of 369 pesticidal, pharmaceutical and other chemicals to wild birds. Toxicol. Appl. Pharmacol. 21:315-330.

Schimmel, S.C., R.L. Garnes, J.M. Patrick, Jr., and J.C. Moore. 1983. Acute toxicity, bioconcentration, and persistence of AC 222, 705, benthiocarb, chlorpyrifos, fenvalerate, methyl parathion, and permethrin in the estuarine environment. J. Agric. Food Chem. 31:104-113.

Schlinke, J.C. 1970. Chronic toxicity of Dursban in chickens, 1969. J. Econ. Entomol. 63:319.

Schlinke, J. C., J. S. Palmer, and L. Hunt. 1969. Preliminary toxicologic study of a phosphorothioate insecticidal compound in turkeys. Am. J. Vet. Res. 30:1705-1709.

Schom, C. B., U. K. Abbott, and N. Walker. 1973. Organophosphorus pesticide effects on domestic and game bird species. Dursban. Poult. Sci. 52:2083.

Smith, G. J. 1987. Pesticide use and toxicology in relation to wildlife: organophosphorus and carbamate compounds. U.S. Fish Wildl. Serv. Resour. Publ. 170. 171 pp.

Smith, G. N. 1966. Basic studies on Dursban insecticide. Down to Earth 22: 3-7.

Smith, G. N. 1968. Ultraviolet light decomposition studies with Dursban and 3,5,6-trichloro-2-pyridinol. J. Econ. Entomol. 61:793-799.

Smith, G. N., B. S. Watson, and F. S. Fischer. 1966. The metabolism of (C^{14})0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate (Dursban) in fish. J. Econ. Entomol. 59:1464-1475.

Streu, H. T., and C. Cruz. 1972. Control of the hairy chinch bug in turfgrass in the northeast with Dursban insecticide. Down to Earth 28:1-4.

Sultatos, L.G., and S.D. Murphy. 1983. Hepatic microsomal detoxification of the organophosphates paraoxon and chlorpyrifos oxon in the mouse. Drug Metabol. Dispos. 11:232-238.

Tagatz, M.E., N.R. Gregory, and G.R. Plaia. 1982. Effects of chlorpyrifos on field- and laboratory-developed estuarine benthic communities. J. Toxicol. Environ. Health 10:411-421.

Thirugnanam, M., and A. J. Forgash. 1977. Environmental impact of mosquito pesticides: toxicity and anticholinesterase activity of chlorpyrifos to fish in a salt marsh habitat. Arch. Environ. Contam. Toxicol. 5:415-425.

Tucker, R.K., and D.G. Crabtree. 1970. Handbook of toxicity of pesticides to wildife. U.S. Fish Wildl. Serv. Resour. Publ. 84:56-57.

Tucker, R. K., and M. A. Haegele. 1971. Comparative acute oral toxicity of pesticides to six species of birds. Toxicol. Appl. Pharmacol. 20:57-65.

Wall, W.J., Jr., and V.M. Marganian. 1971. Control of Culicoides melleus (coq.) (Diptera: Cercetopogonidae) with granular organophosphorus pesticides and the direct effect on other fauna. Mosq. News 31:209-214.

Wall, W. J., Jr., and V. M. Marganian. 1973. Control of salt-marsh culicoids and tabanus larvae in small plots with granular organophosphorus pesticides. Mosq. News 33:88-93.

Washino, R. K., W. Ahmed, J. D. Linn, and K. G. Whitesell. 1972. Rice field mosquito control studies with low volume Dursban® sprays in Colusa County, California. IV. Effects upon aquatic nontarget organisms. Mosq. News 32:531-537.

Windholz, M. (ed.). 1976. The Merck Index, ninth edition. Merck and Co., Rahway, New Jersey.

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. Biological Report 85(1.13)	2.	3. Recipient's Accession No.
4. Title and Subtitle Chlorpyrifos hazards to fish, wildlife, and invertebrates: a synoptic review			5. Report Date March 1988
			6.
7. Author(s) E. W. Odenkirchen and R. Eisler			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Patuxent Wildlife Research Center U.S. Fish and Wildlife Service Laurel, MD 20708			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered
			14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$), an organophosphorus compound with an anticholinesterase mode of action, is used extensively in a variety of formulations to control a broad spectrum of agricultural and other pestiferous insects. At recommended application rates many species of nontarget organisms--including fish, birds, and invertebrates--have experienced deleterious effects. Sensitive species of aquatic biota died at nominal water concentrations between 0.035 and 1.1 ug chlorpyrifos/l. Acute oral toxicity to sensitive species of birds ranged between 5 and 13 mg chlorpyrifos/kg body weight; for mammals, this was 151 mg/kg body weight.

Proposed criteria and research needs to protect fishery and wildlife resources are presented.

17. Document Analysis a. Descriptors

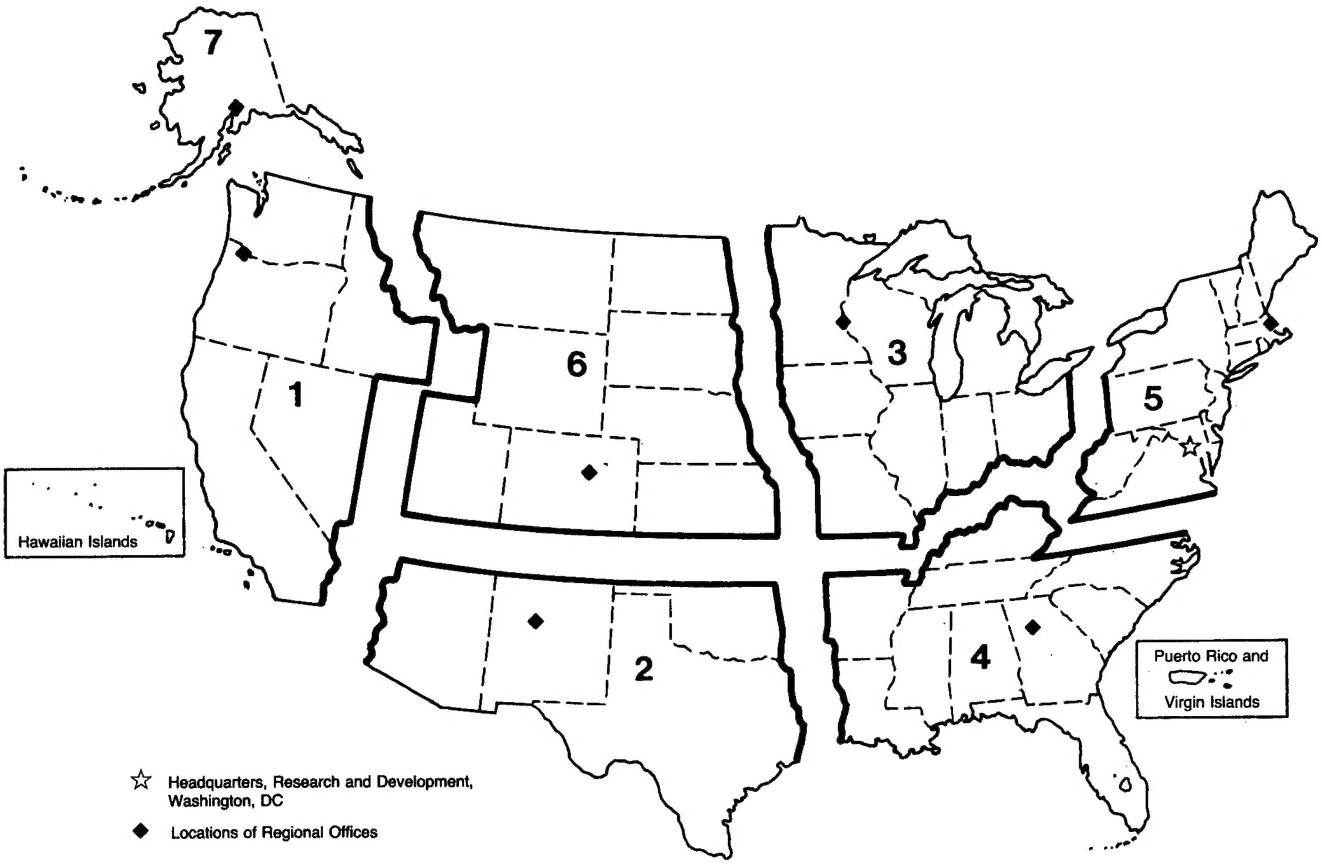
Pesticides	Fishes
Contaminants	Wildlife
Toxicity	Natural resources

b. Identifiers/Open-Ended Terms

Chlorpyrifos	Organophosphorus insecticide
Dursban	Metabolism
Lorsban	Sublethal effects

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report) Unclassified	21. No. of Pages 34
Unlimited distribution	20. Security Class (This Page) Unclassified	22. Price



REGION 1
Regional Director
U.S. Fish and Wildlife Service
Lloyd Five Hundred Building, Suite 1692
500 N.E. Multnomah Street
Portland, Oregon 97232

REGION 2
Regional Director
U.S. Fish and Wildlife Service
P.O. Box 1306
Albuquerque, New Mexico 87103

REGION 3
Regional Director
U.S. Fish and Wildlife Service
Federal Building, Fort Snelling
Twin Cities, Minnesota 55111

REGION 4
Regional Director
U.S. Fish and Wildlife Service
Richard B. Russell Building
75 Spring Street, S.W.
Atlanta, Georgia 30303

REGION 5
Regional Director
U.S. Fish and Wildlife Service
One Gateway Center
Newton Corner, Massachusetts 02158

REGION 6
Regional Director
U.S. Fish and Wildlife Service
P.O. Box 25486
Denver Federal Center
Denver, Colorado 80225

REGION 7
Regional Director
U.S. Fish and Wildlife Service
1011 E. Tudor Road
Anchorage, Alaska 99503

TAKE PRIDE IN AMERICA

Preserve Our Natural Resources

DEPARTMENT OF THE INTERIOR
U.S. FISH AND WILDLIFE SERVICE

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.